

HYDROCARBON FUEL PROCESSOR CATALYST

This invention relates to a hydrocarbon fuel processor catalyst for converting or reforming a hydrocarbon fuel into a simple fuel and is more especially, although not
5 exclusively, concerned with a catalyst for converting a liquid hydrocarbon fuel to hydrogen for use in a fuel cell.

Fuel cells offer the promise of smaller and lighter weight power sources that are potentially instantaneous and silent in their operation. For example, fuel-cell powered
10 vehicles are currently being developed as a more fuel-efficient and less polluting alternative to the internal combustion engine.

For large scale, generally static applications, solid oxide fuel cells can be used. Due to their high operating temperature, typically around 800°C, such fuel cells are able to
15 directly utilise fuels such as methanol, methane or natural gas. Whilst suitable for large scale operation, such as combined heat and power facilities for building complexes, these cells are not suited to mobile applications as they are bulky and have a slow start up due to their high operating temperature.

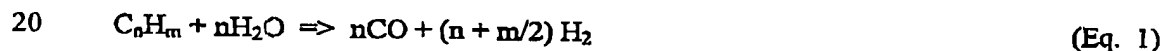
For mobile applications such as vehicles, polymer fuel cells have been proposed. Due to their relatively low operating temperature (typically around 80°C), such cells offer
20 a rapid start up as required in these applications. Polymer fuel cells operate most efficiently on pure hydrogen, but it is currently difficult to store hydrogen on board the vehicle in a safe and cost effective way. A fuel processor or reformer converts

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hydrocarbon fuels to hydrogen gas, potentially enabling fuel-cell powered vehicles to run on fuels which are widely available today, such as liquefied petroleum gas (LPG), paraffin, gasoline or diesel.

5 Compact fuel processors suitable for use on vehicles have already been developed for lighter hydrocarbon fuels such as methanol. However, these processors are usually specific to one type of fuel and require a high purity feed since impurities such as sulphur are very detrimental to the reforming catalyst and can permanently deactivate it. It is therefore desirable to produce a compact fuel processor that can extract
10 acceptable amounts of hydrogen from a wide range of commercial fuels and function without adjustment as the fuel type changes. These new reforming catalysts should be much more resistant to coking or sulphur deactivation than the currently available catalysts.

15 A number of different designs of fuel processor have been proposed for converting hydrocarbon fuels to hydrogen which are based on a steam-reforming reaction in which vaporised hydrocarbon fuel is reacted with steam (H₂O). This reaction can be represented by the following endothermic equation:



A catalyst may optionally be used to increase the reaction rate, though high temperatures and pressures are still required. As can be seen from the equation, the carbon in the hydrocarbon fuel is converted to carbon monoxide by oxidation using

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the oxygen provided by the steam whilst the hydrogen in the fuel and steam is released as hydrogen gas. The optimum steam to carbon ratio ($\text{H}_2\text{O}:\text{C}$) depends on the processor conditions (temperature and pressure), but invariably this ratio increases as the carbon content of the hydrocarbon increases. Large quantities of steam are therefore required for heavy fuels such as diesel and this demands a high energy input to vaporise the water, leading to a poor thermal efficiency, a slow response time and a slow start up from cold.

An alternative, potentially more responsive, process relies upon the partial oxidation of the hydrocarbon fuel. This can be represented by the following exothermic reaction:



The optimum oxygen to carbon ratio ($\text{O}_2:\text{C}$) depends on the processor conditions and increases as the carbon content of the hydrocarbon increases. Again a catalyst can be used to increase the reaction rate. To prevent clogging of the catalyst, most typically by coke deposition, the initial combustion can occur at high temperatures in the absence of a catalyst to break the hydrocarbon fuel down to simpler molecules. The gas stream is then passed over a catalyst to further break down the molecules into carbon monoxide and hydrogen. Although such a processor exhibits a faster response it has relatively lower hydrogen conversion efficiency than a steam reforming system.

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It has been further proposed to provide fuel processors which use an "autothermal reforming process" to convert the hydrocarbon fuel to hydrogen and carbon monoxide with a combination of the above two processes. In such a processor the heat liberated by the exothermic partial oxidation reaction (Eq. 2) is used to drive the endothermic steam reforming reaction (Eq. 1) thereby improving the overall thermal efficiency of the processor. Different specialist catalysts may be used in physically separate partial oxidation and steam reforming reaction volumes within the processor or alternatively the partial oxidation and steam reforming reactions can take place over a common catalyst bed. The latter produces a simpler system design but places great demands on the catalyst material. In one known design the vaporised fuel is mixed with air and steam and then injected into an enclosure containing the granulated catalyst material.

At present the known fuel processors capable of processing heavier hydrocarbons fuels such as diesel are not ideally suited to small scale mobile applications. Firstly, the endothermic nature of the steam generating and steam reforming processes does not readily lend itself to operating efficiently on a small scale. Secondly, the comparatively high carbon content (high carbon to hydrogen ratio C:H) of many hydrocarbon fuels such as diesel clogs the catalyst through the deposition of coke (carbon) on the surface of the catalyst which blocks access to the active surface of the catalyst. Thirdly, the high sulphur level in many heavier hydrocarbon fuels poisons, that is reduces the activity of, the known catalysts used in the steam-reforming process thereby degrading the conversion efficiency.

The known catalysts for fuel conversion, or reforming, comprise base metals (such as nickel), noble metals (such as platinum), or a mixture of these, either in powdered form or as a coating on the surface of an inert ceramic substrate. The noble metal is generally dispersed in the form of small particles in order to minimise the metal cost and maximise the surface activity. These catalysts are, however, adversely affected by sulphur present in the fuels and are vulnerable to coking since there is no mechanism to remove the carbon from the catalyst surface once it has been deposited. There is therefore considerable scope for the development of improved catalyst systems that are cheaper, more efficient and more versatile than the current materials.

The present invention has arisen in an endeavour to develop a new catalyst formulation which is suitable for use with diesel and other heavy hydrocarbon fuels in an autothermal fuel processing system, and which is in part at least resistant to both sulphur poisoning and clogging with coke deposition.

According to the present invention there is provided use of a rare earth metal cobalt oxide ($MCoO_3$) having the perovskite crystal structure as a catalyst in a hydrocarbon fuel processor for converting or reforming a hydrocarbon fuel into a simple fuel most especially hydrogen. Due to its high oxygen ion mobility at temperatures at which such fuel processors operate, typically less than 800°C , use of such a catalyst offers a number of advantages over the known catalysts: (i) the presence of the oxygen ions at the catalyst surface coating promotes the fuel breakdown process; (ii) the oxygen ions oxidise any carbon or contaminants which may be deposited on the catalyst surface coating during the fuel breakdown reaction and this reduces the likelihood of the catalyst becoming clogged, especially when using a high C:H fuel such as diesel, and

(iii) the oxygen ions prevent contaminants which might otherwise de-activate the catalyst, such as sulphur, becoming bonded to the surface coating. The inventors further believe that during the use of the catalyst the surface decomposes and becomes covered with a catalytically active coating of rare earth oxide, hydrated rare-earth oxide and cobalt metal particles which prevents the catalyst's activity becoming rapidly degraded by carbon deposition and/or by the effects of sulphur or other contaminants. A catalyst in accordance with the invention can therefore be said to be self cleaning. In contrast the known catalysts comprise an inert support structure with a catalytically active coating which is vulnerable to the effects of carbon and/or sulphur.

Advantageously the catalyst further includes a noble metal or noble metal oxide. Such a catalyst offers a high catalytic activity in which the oxygen ions provide a scouring activity which protects the activity of the noble metal or noble metal oxide at the operating temperature of the fuel processor. In one embodiment the noble metal or noble metal oxide comprises platinum or platinum oxide. In a particularly preferred embodiment the noble metal or noble metal oxide comprises ruthenium or ruthenium oxide which is found to give at least the same activity but which has a cost appreciably less than that of platinum. Preferably the noble metal or noble metal oxide is present up to 2 mole %.

Preferably the catalyst further comprises a solid solution having the perovskite crystal structure of the rare earth metal cobalt oxide and an alkaline earth metal cobalt oxide, such as for example a solid solution of lanthanum cobalt oxide and strontium cobalt

oxide. The substitution of the rare earth ions by alkaline earth ions increases the number of vacant sites for oxygen within the perovskite crystal structure thereby increasing the number and the mobility of oxygen ions within the crystal lattice. Advantageously the alkaline earth metal cobalt oxide is included in a proportion of up to 50%.

In a preferred catalyst composition the alkaline earth metal comprises strontium although calcium or barium can be used.

According to a second aspect of the invention a hydrocarbon fuel processor catalyst is characterised by comprising a rare earth metal cobalt oxide having the perovskite structure as described above. According to a third aspect of the invention a hydrocarbon fuel processor for converting a hydrocarbon fuel to hydrocarbon incorporates a catalyst as described above.

Nine catalyst compositions in accordance with the invention will now be described by way of example only. The first catalyst composition described is lanthanum cobalt oxide (LaCoO_3) having the perovskite crystal structure. Lanthanum oxide (La_2O_3) powder was heated in air at 1000°C to decompose any Lanthanum Hydroxide $\text{La}(\text{OH})_3$ present in the material to give single phase La_2O_3 . The single phase La_2O_3 material was mixed with cobalt oxide (CoO) powder in appropriate weights to give the LaCoO_3 and the mixture ball-milled for 4 hours in approximately 40 gramme batches and then calcined (heated in a furnace) in air at 1050°C for 3 hours. The ceramic product after calcining was crushed and graded into a desired particle size,

approximately 1-10 μ m, prior to testing. As will be appreciated by those skilled in the art, the desired particle size will depend on the type of fuel processor and can accordingly be readily optimised for a required application.

5 X-ray diffraction studies of the material showed the crystal structure to be a substantially phase pure perovskite crystal structure. The perovskite crystal structure is that which exists in mineral perovskite CaTiO₃ and which is commonly adopted in compounds having the general formula ABO₃ where A is a relatively large cation (lanthanum in this example) and B is a relatively smaller cation (cobalt in this
10 example). The B cations are each surrounded by a maximum of six oxygen ions to form a three-dimensional network of corner shared octohedra whilst the A cations occupy the interstices between the octohedra. The facile mixing of cations with different valences on both the A and B sites combined with the variable valence nature of the B cations promotes a complex defect structure which can provide a high
15 mobility for the oxygen ions. X-ray diffraction patterns of samples showed that a significant quantity of La₂O₃ still remained in the samples which could not be eliminated by calcining for longer periods. This is believed to be a consequence of the CoO actually being a mixture of CoO and Co₃O₄, the latter of which cannot be readily converted to single CoO by heat treatment. To compensate for this a 5 mole
20 % excess of CoO was added to the starting mixture. Samples prepared in this way showed only a trace of La₂O₃ remaining in the final composition.

Eight other catalyst compositions were synthesised which are shown in Table 1 below. First, samples were prepared containing the noble metals ruthenium (Ru) and

platinum (Pt) by calcining mixtures of La_2O_3 , and PtO_2 or RuO_2 with a 5 mole % excess of CoO (compositions 2 and 3 in the table). Scanning electron microscopy analysis of the platinum oxide and ruthenium oxide powders showed that it was an extremely fine powder with a primary particle size probably well below $0.1\mu\text{m}$ (dimensions beyond the resolution of the scanning electron microscope equipment available at the time of analysis). The energy-dispersive X-ray analysis in a scanning electron microscope of single grains of the resultant catalyst material confirmed that the platinum/ruthenium was present either within the grains or as a coating on the surface of the grains. No particles could be identified which were very rich in platinum/ruthenium, suggesting that the noble metal is not present as a second phase (either as the metal or as the oxide).

Catalysts containing the noble metal and/or noble metal oxide were found to exhibit an enhanced activity compared to LaCoO_3 . This is attributed to the catalytic activity of the noble metal which is protected against clogging and or contamination by the scouring effect of the high mobility oxygen ions from the LaCoO_3 perovskite crystal structure. This being said it will be appreciated that the concentration of noble metal is selected such that there is sufficient LaCoO_3 to provide adequate cleaning of the metal. Test results indicate that ruthenium is at least as effective as platinum but has the substantial advantage of being much lower in cost.

Composition 1 LaCoO_3	Composition 4 $\text{La}_{0.75}\text{Sr}_{0.25}\text{CoO}_3$	Composition 7 $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$
Composition 2 LaCoO_3 + 2 mole % PtO_2	Composition 5 $\text{La}_{0.75}\text{Sr}_{0.25}\text{CoO}_3$ + 2 mole % PtO_2	Composition 8 $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ + 2 mole % PtO_2
Composition 3 LaCoO_3 + 2 mole % RuO_2	Composition 6 $\text{La}_{0.75}\text{Sr}_{0.25}\text{CoO}_3$ + 2 mole % RuO_2	Composition 9 $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ + 2 mole % RuO_2

Table 1: Catalyst compositions.

In the remaining compositions (4 to 9), a fraction of the lanthanum ions was replaced by strontium (Sr) ions to form a solid solution of LaCoO_3 and SrCoO_3 . A 5 mole % excess of CoO was also added to the starting mixtures of these compositions. The calcination temperature needed for the complete elimination of La_2O_3 decreased as the strontium content increased, and was found to be 950°C for $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$. The complete list of synthesized samples is given in Table 1. The substitution of the lanthanum ions by strontium ions increases the number of vacant sites for oxygen within the perovskite structure thereby increasing the number and the mobility of oxygen ions within the crystal lattice.

Testing of the catalysts with diesel and other hydrocarbon fuels in a fuel processor showed the material to have good catalytic activity which was resistant both to clogging by coke or other contaminants and to poisoning from sulphur. The following results pertain to Composition 3 in the above Table 1. This composition was tested with a range of liquid hydrocarbon fuels including liquid petroleum gas (LPG – a mixture of propane and butane), paraffin, gasoline and diesel.

As far as possible, the same test procedure was used for each of these fuels. The steam to carbon ratio ($H_2O:C$) and air to carbon ratio ($O_2:C$) ratios were fixed during initial temperature-programmed tests. The feed temperature was then ramped up from approximately 350°C to 850°C and then back down to 350°C, while the hydrogen (H_2), carbon monoxide (CO), carbon dioxide (CO_2), methane (CH_4) and heavier hydrocarbon content of the dried output gas stream were measured. The aim was to determine whether coke deposition or deactivation with sulphur occurred over a portion of the temperature ramp. For example, coke deposition often occurred at low temperatures but was normally burnt off by the catalyst at higher temperatures. The plot of the hydrogen content versus temperature then showed a hysteretic effect where, at a selected feed temperature, the hydrogen content was lower when the catalyst temperature was raised than when the catalyst temperature was lowered.

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Following the temperature ramp, the temperature of the fuel, air and steam feed was held constant at selected values, typically 600°C or 800°C. The composition of the feed, that is steam to carbon ratio ($H_2O:C$) and air to carbon ratio ($O_2:C$), more especially the ratio of the oxygen content of the air to carbon, were then altered and

the measurements repeated to determine the conditions providing the best catalytic activity. The steam and air to carbon ratios used are shown in Table 2. These conditions were chosen because they resulted in the near autothermal conversion of the heavier liquid fuels (paraffin, gasoline and diesel).

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H ₂ O:C	O ₂ :C
1.0	0.38
1.5	0.50
2.0	0.64

Table 2: Steam (H₂O:C) and air (O₂:C) to carbon ratios used for the catalyst tests.

The results obtained are summarised in Table 3. These data were obtained while the feed temperature was held at a constant value, and shows the hydrogen (H₂), carbon monoxide (CO) and methane (CH₄) content of the output gas stream under the conditions that generated the highest hydrogen content for each tested fuel. As is discussed below the remainder of the output gas stream comprises nitrogen and carbon dioxide the former resulting from the use of air rather than oxygen in the reaction process. In general, this occurred under near autothermal conditions using a H₂O:C ratio of 1.0 and a O₂:C ratio of 0.38. However, the use of LPG under these conditions gave very high reactor temperatures in excess of ~1000°C. The use of a higher H₂O:C ratio and a lower O₂:C ratio is therefore beneficial with this fuel since

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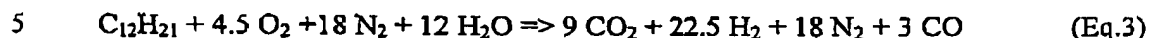
this maintained the catalyst bed at a lower temperature and also increased the concentration of hydrogen in the output gas stream

Fuel	Test Results				Test Conditions		
	% content of output gas stream			Catalyst temp. (°C)	O ₂ :C	H ₂ O:C	Feed temp. (°C)
	H ₂ max.	CO	CH ₄				
LPG	32.9	11.8	1.2	1007	0.38	2.0	600
	28.1	12.9	2.0	980	0.38	2.0	800
Paraffin	40.5	10.1	0.5	587	0.38	1.0	600
	35.2	15.2	2.6	758	0.38	1.0	800
Unleaded gasoline	13.5	7.6	0.9	743	0.50	1.0	600
	21.6	13.2	3.7	781	0.38	1.0	800
City diesel	34.9	9.5	0.6	594	0.38	1.0	600
	32.5	13.9	2.4	755	0.38	1.0	800

5 Table 3: Test results and test conditions for various hydrocarbon fuels using the catalyst composition 3.

10 The small concentrations of fuel or other hydrocarbons exiting the reactor (less than 5%) indicate that near complete conversion was obtained for LPG, paraffin and diesel. For all of these fuels, the maximum hydrogen content under these conditions is calculated to fall within the range 42%-48%. Taking diesel as an example, the

average molecular weight of this fuel is assumed to be ~170 and the chemical composition approximates to $C_{12}H_{21}$. For $H_2O:C = 1$ and $O_2:C = 0.38$, the reaction stoichiometry for complete conversion would then be:



The composition of the reformat would therefore be:



so that the maximum hydrogen content extractable from this fuel under these conditions is ~43%.

15 The conversion efficiency for gasoline was lower than that of the other tested fuels, and this is attributed to the higher sulphur content of this fuel. The LPG, paraffin and city diesel had a very low sulphur contents (less than 10ppm) while the unleaded gasoline had a much higher sulphur content of 100ppm. However, the temperature programmed data obtained with gasoline indicate that retained sulphur species on the catalyst surface desorbed at high temperatures around 800°C so that operation under
20 these conditions at least partially restored the catalytic activity.

The inventors believe that the good catalytic properties of these materials are due to their high oxygen ion mobility at temperatures for use in such fuel processors, typically less than 800°C. Firstly the presence of the oxygen ions at the catalyst

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surface promotes the fuel breakdown process. Secondly the oxygen ions oxidise any carbon or contaminants which may be deposited on the catalyst surface during the fuel breakdown reactions thereby reducing the likelihood of catalyst clogging, especially when using a fuel having high carbon to hydrogen ratio such as diesel.

5 Thirdly the oxygen ions prevent contaminants, such as sulphur, becoming bonded to the surface which might otherwise de-activate the catalyst. It is believed that during the use of the catalyst a certain degree of decomposition of the Perovskite crystal structure occurs at the material surface such that the surface of the material becomes covered with a catalytically active coating of lanthium oxide (La_2O_3) and cobalt metal
10 particles which prevents the catalyst's activity becoming rapidly degraded by carbon deposition and/or by the effect of sulphur or other contaminants.

It will be appreciated that the present invention is not limited to the specific compositions described and that further compositions are envisaged which are within
15 the scope of the invention. For example the basic catalyst has been described in relation to LaCoO_3 though other rare earth metal (M) cobalt oxides (MCoO_3) having the perovskite crystal structure could be used. Furthermore it is envisaged to add other noble metals or noble metal oxides or a mixture thereof. Further it will be appreciated that solid solutions with alkaline earth metals other than strontium such
20 as calcium or barium can be used to increase the oxygen ion mobility. Furthermore it will be appreciated that a catalyst in accordance with the invention can be used for other types of hydrocarbon fuels other than diesel and is especially suited to use with heavier hydrocarbon fuels.

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